

RECOVERY BEHAVIOR OF HARDNESS INDENTATIONS OF EPOXY- REINFORCED HYBRID FILLER

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ABSTRACT

Modern studies demonstrated that a cogent amendment “in mechanical properties of thermosetting polymers” maybe carried out by adopting submicron fillers. Mono composites (epoxy/wollastonite) and hybrid composites (epoxy/wollastonite-beeswax) were prepared and, the elastic and viscoelastic recovery of the resultant composites were accomplish. It was established that the partial encapsulation of wollastonite by beeswax could be upgraded the compatibility between wollastonite and epoxy resin which resulting in an advancement in epoxy composite mechanical properties. The elastic modulus for the composite reinforced with percentage 2% of wollastonite increased by 12% comparing with pure epoxy, while the presence of beeswax can significantly improve the elastic modulus by 67% and 101% for the 2% wollastonite loading with a 4:1 and 2:1 ratio of wax beeswax respectively.

The elastic recovery percent decreased with increasing the percentage of wollastonite in the composite, where it has decreased from 58% for the pure epoxy to the 13.3% for the epoxy reinforced with 5%. A great enhancement in elastic recovery, 91.6% and 85.4% for the 2% wollastonite loading with a 4:1 and 2:1 ratio of wax beeswax respectively.

KEYWORDS: Hybrid Composite, Elastic, Viscoelastic Recovery, Wollastonite & Beeswax

Received: Jul25, 2018; **Accepted:** Aug 15, 2018; **Published:** Sep14, 2018; **Paper Id.:** IJMPERDOCT201842

INTRODUCTION

There were numerous publications in recent years with regards to hybrid polymer composites (Xia et al, 2010; Chiang and Hsu 2010; Wang et al, 2010; Gururaja and Hari Rao 2012; Rostamiyan et al, 2014). The possibility of developing new materials with greater rigidity and impact resistance represents the main reason behind the interest in this approach. Hybrid composites employ the advantages of the individual components to reduce the defects arising from their detach use (Joshi and Purnima 2010; Davoodi et al, 2010). Hybrid composites have many advantages such as given balanced thermal stability, reduced weight and cost, balanced strength, and stiffness, better fatigue resistance, impact resistance, fracture toughness besides reducing notch sensitivity (Joshi and Purnima 2010).

For most polymeric materials, the impressions produced by the indenter would not be constant in shape, but they would recover with time, due to its complex viscoelastic nature (Lorenzo et al, 1988). The environmental resistance and long-term durability represent a crucial factor in the applications, where the polymeric materials used in structural parts (Yuan et al, 2008). Hence, the hardness can appear as a pointer for the permanent deformation processes, which designate the test material. In spite of the indentation stresses are highly concentrated in the plastic zone in surrounding close to the contact, in any case, an expanding at a considerable,

level into the away beyond the elastic matrix. That is, the hardness is accurately an elastic-plastic parameter (Lawn and Howes 1981). The ratio of the summit normal load to the subjected area of the impression represents the hardness of the material (Lorenzo et al, 1988). The reversible and irreversible components of contact deformation might be predicted to have relative significance in the elastic recovery during unloading of the indenter (Lawn and Howes 1981).

Due to a perfect electric insulating, good chemical stability and relatively minimal shrinkage during cure, and ease in processing, the epoxy resin has a lot of industrial applications like adhesives or matrices for composites. As compared epoxy with metals, the low stiffness, and average mechanical properties represent the principal problems with the epoxy resins for engineering apps, to surmount these problems reinforcement agents such as coconut-shell powder, Portland cement and potassium titanate bristles have been used to reinforced epoxy (Alok et al, 2013; Panzera et al, 2010).

Literature survey reveals a large number of inorganic materials (silica, talc, graphite, and montmorillonite clay) are being used as fillers in polymer composites (Katz and Milewski 1987). Varadarajulu et al, studied the epoxy-UP resin blend were completely miscible, using viscosity, ultrasonic velocity and refractive index methods (Varadarajulu et al, 2003). From the literature it was found that Wollastonite is a calcium silicate mineral, basically used in ceramics, friction products (brakes & clutches) metal making, paint filler and plastics (Varadarajulu et al, 2001).

The current work is a study the recovery behavior of epoxy composites, enabling a definitive evaluation of indentation hardness characterization of polymers and a quantitative estimation of viscoelastic recovery at deformed surfaces of the epoxy composite, and to determine which is the best reinforcing manner to enhance the elastic recovery of epoxy using hybrid filler.

MATERIALS AND METHODS

Material

The epoxy resin diglycidylether of bisphenol A (DGEBA), and the curing Agent cycloaliphatic polyamine. The mass ratio between the resin and curing agent was set at 1:2. Wollastonite is a kind of calcium metasilicate mineral salt. Its chemical formula is $\text{CaO} \cdot \text{SiO}_2$. Beeswax (Ceraalba) it is a inbred wax produced by honeybees of the genus *Apis*, which has a chemical formula $\text{C}_{15}\text{H}_{31}\text{COOC}_{30}\text{H}_{61}$. Beeswax has a low melting point range of 62 °C to 64 °C (144 °F to 147 °F). If beeswax is heated above 85 °C (185 °F) discoloration occurs. It has flash point at 204.4 °C (400 °F) and density at 15 °C is 958 kg/m³ to 970 kg/m³.

Composite Production

To prepare the composites material, two different types of fillers were chosen, first wollastonite needle shape particle and the second is beeswax filler, where they were mixed with a variety weight percentages into the epoxy matrix. All the composites were prepared by mechanically mixing with a high shear laboratory-mixing equipment. In order to remove the moisture, heating system at 70 °C under vacuum were used to drying wollastonite particles for several hours before utilized.

In order to lower the viscosity during the mixing process also to enable a preferable wetting of the filler, epoxy resin preheated at 70 °C and then the filler was incorporating into the resin using a mechanical stirrer and keeps the resultant mixture under vacuum for 15 minutes to eliminate the entrapped air. Then the curing agent is added to the mixture with gentle stirring for 15 min followed by curing for several hours in an oven at 100 °C. The test specimens can be machined from the cured composite sheets. Regarding hybrid composites, a variety percentage of beeswax were blended

with 2% wollastonite using the same above steps Table 1.

Table 1: Code and the Ratio of the Materials used for Samples Production

N. of Sample	Composition
SA0	Pure Epoxy
SA1	Epoxy/0.5% Wollastonite
SA2	Epoxy/1% Wollastonite
SA3	Epoxy/2% Wollastonite
SA4	Epoxy/5% Wollastonite
SB1	Epoxy/(2% Wollastonite & 0.5% Beeswax)
SB2	Epoxy/(2% Wollastonite & 1% Beeswax)
SB3	Epoxy/(2% Wollastonite & 2% Beeswax)

RESULTS AND DISCUSSIONS

FTIR Test

FTIR tests showed that the C-O deformation band is concentrated at 915 cm^{-1} , and in both cases, the 3050 cm^{-1} C-H stretching band for terminal oxirane group was observed. The broadband at 3500 cm^{-1} is appointed to O-H stretching of hydroxyl groups, divulged the existence of dimers or high molecular weight types, as well as, the bands located at $1000\text{--}1100\text{ cm}^{-1}$ matching to the ether linkage. In general, FTIR tests do not indicate the presence of chemical bonds between the wollastonite and epoxy matrix as well as between beeswax and epoxy and may be limited to the emergence of physical bonds have a clear role in linking the filler with the epoxy matrix Figure (1).

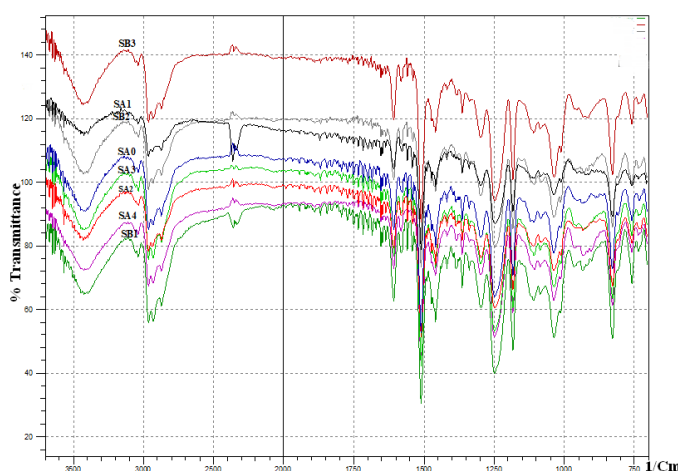


Figure 1: FTIR Analysis of Pure Epoxy, Epoxy Reinforced with Wollastonite Particles and Epoxy Reinforced with Wollastonite/Wax Hybrid Filler, (Samples Production are Shown in Table 1).

Bending Tests

The flexural test measures according to ASTM D7264M – 15 using the force demanded to bend a beam under three-point loading conditions. Flexural modulus is utilized as a marker of a material's stiffness when flexed, using the equipment Universal Tester, Flexural test fixtures. Specimen size is chosen such that the flexural properties are determined accurately from the tests. Specimen thickness is 5 mm and the standard specimen width is 10 mm with the specimen length being about 80 mm. Three points for bending testing is done to calculate the elastic modulus of the composite materials. The results showed that the elastic modulus increases with increasing the percentage of wollastonite, the module might

decrease when more wollastonite was added, these may be due to agglomerate the filler at high concentration Table 2.

Table 2: The Flexure Moduli of Epoxy and Epoxy Composites

N. of Sample	Elastic Modulus(Mpa)	Hardness (Shore D)
SA0	1200	70
SA1	1800	72
SA2	1850	72
SA3	1340	75
SA4	1065	71
SB1	2010	72.5
SB2	2500	71
SB3	1700	73

The mechanical properties of the composite could be influenced by blending the epoxy/ wollastonite composite with a variable percentage of beeswax. A considerable upgrading in elastic modulus for the epoxy reinforces with 2% wollastonite/ (0.5, 1 and 2%) beeswax as a hybrid filler, due to existence wax layer on the wollastonite surfaces, which allow more wollastonite, surfaces to be exposed for bonding to the epoxy matrix. The above results support the belief that wollastonite encapsulation by the beeswax was an effective way to improve the dispersibility of wollastonite in the epoxy matrix, while still permitting for a bridge between the wollastonite and the matrix (epoxy) for bonding and reinforcement Table 2.

Hardness Test

Such as many other hardness tests, durometer is a measuring the depth of an indentation in the material generated by an applied force on a standardized presser foot. The residual depth in the material depends on the hardness of the material, its viscoelastic properties, the form of the presser foot, and the duration of the test. The initial hardness or the indentation hardness after a specific time are characterized using ASTM D2240 durometers. As illustrated in the Table 2, the hardness of the composites slightly increased with increasing the percentage of wollastonite, this may be due to the presence of hard wollastonite particles in the matrix and the subsequent chain interlocking which enhance the ability to resist indentation comparing with the pure matrix. It should be noted that the hardness is reduced at the relatively high percentage of wollastonite (5 wt. %). This attributed to the improper bonding at a relatively high concentration which leading to agglomeration of the particles and lowering of the hardness, on the other hand, with the presence of beeswax in the hybrid composites, there is no significant change in the hardness of the resultant composites.

Recovery Test

The elastic and viscoelastic recovery of the epoxy composites was evaluated by the percentage of recoverable strain measured after penetration without any external effect during a conventional hardness test. All samples indented with the same load using shore D hardness tester, where the primary penetration depth (h_0) after 5 seconds measured and the residual depth (h_r) after 24 hr. also measured at room temperature Figure 2. The recovery percentage was calculated from the following equation:

$$\text{Recovery \%} = \frac{h_0 - h_r}{h_0} * 100\%(1)$$

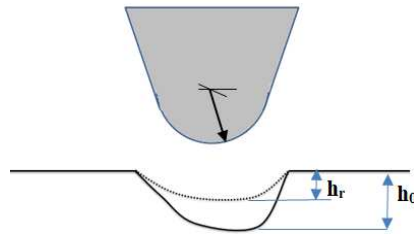


Figure 2: Indented Surface

Figure 3 shows the results of the optical microscope for pure epoxy samples and for the epoxy composites reinforced with a variety weight percentage of wollastonite (0.5, 1, 2 and 5). The results showed that the elastic recovery percent decreased with increasing the percentage of wollastonite in the composite, where it is decreased from 58% for pure epoxy to the 13.3% for the epoxy reinforced with 5% Table 2, this behavior due to increasing the brittleness of the composites that increases the plastic component in the elastic-plastic behavior.

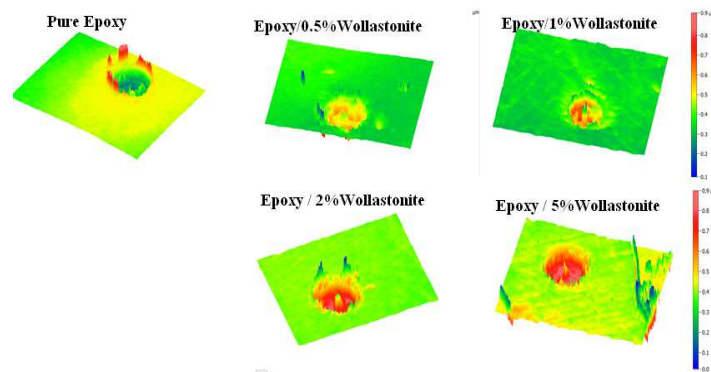


Figure 3: Optical Microscope Images for Pure Epoxy Samples and for the Epoxy Composites Reinforced with a Variety Weight Percentage of Wollastonite

The results for composites, reinforced Hybrid filler were prepared by introducing different percentages of beeswax with epoxy composite reinforced with 2% wollastonite, showed a great enhancement in elastic recovery. 91.6% and 85.4% for the epoxy reinforced with hybrid filler (2% wollastonite and 0.5% beeswax) and (2% wollastonite and 1% beeswax) respectively due to develop the mechanical performance of the composites and perhaps the presence of wax had the effect of improving the recovery behavior of polymer chains due to enhancing their mobility and increasing the elasticity component in the elastic-plastic behavior of the polymer. While further increases in the percentage of wax to caused decreasing the modulus and elastic recovery less than pure epoxy.

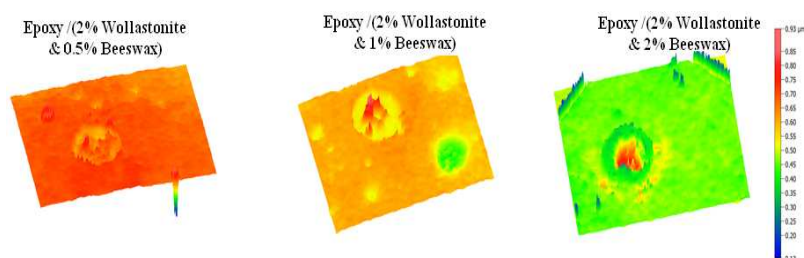


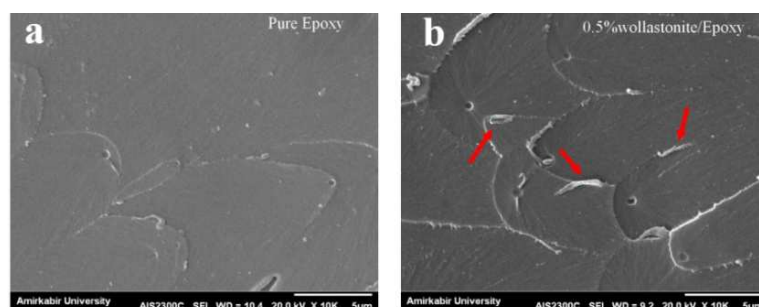
Figure 4: Optical Microscope Images for the Epoxy Composites Reinforced with a Variety Weight Percentage of Hybrid Filler

Table 3: The Recovery of Epoxy and Epoxy Composites

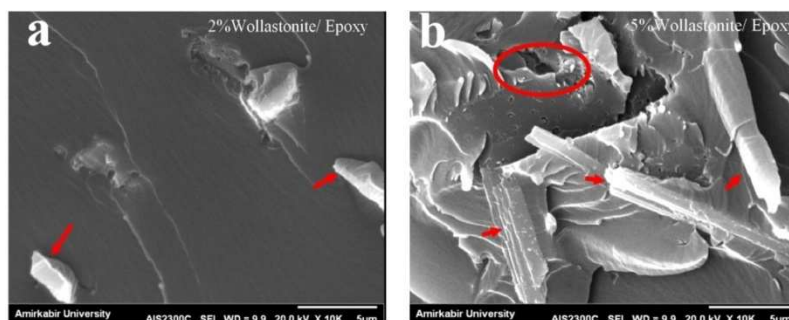
Sample	SA0	SA1	SA2	SA3	SA4	SB1	SB2	SB3
% Recovery	58	52	31.8	13.9	13.34	91.6	85.4	30

SEM Studies

The images of scanning electron microscope for the fracture surfaces of the epoxy composite gave an exact description about the distribution of wollastonite in the epoxy matrix and maybe the adhesion bonding between them. SEM images implied that the pure epoxy has a smooth fracture surface which indicating a typical brittle rupture. After the addition of 0.5% of wollastonite, sea waves radiating fracture patterns were displayed (Figure 5b), which propose an improved ductile rupture to some degree.

**Figure 5: The Fracture Surface of the a) SA0 b) SA1**

Further increasing in wollastonite, causes an increment in brittleness of the epoxy matrix, which leads to open the micro-cracks easily. After accumulate and merge these cracks to form longitudinal cracks along the fiber and then the failure of the composite. The damage may initiate the striations/microscopic cracks (crazing) in the matrix or at the filler/matrix interface. When these cracks reached to a certain number and size, they will tend to integrate to form macroscopic matrix cracks Figure 6.

**Figure 6: The Fracture Surface of the a) %SA2 b) SA3**

The use of hybrid filler (wollastonite with a variety of wax) had a clear effect in improving the dispersibility of the wollastonite within the epoxy matrix and thus changing the fracture behavior of the surface from plastic deformation to the smooth surface where, this may be due to encapsulate the surface of the wollastonite with beeswax, which makes it completely covered with epoxy matrix. On the other hand, it is clear that the most effective wax percentage was 0.5 %, which showed improving the mechanical performance of the produced composite, as well as improved elastic and viscoelastic recovery.



Figure 7: The Fracture Surface of the a) %SB1 b) SB2 c) SB3

Further increasing in beeswax percentage typically 1 and 2% caused an appearance of non-mixed wax layers with the epoxy matrix in the surface of the fracture and this may be the causes for the lower recovery of the resulting compound.

CONCLUSIONS

According to the experimental tests, the results of FTIR showed that there are no chemical bonds between the epoxy matrix and wollastonite as well as with beeswax and epoxy. The elastic modulus for the composite increased with increasing the percentage of wollastonite comparing with pure epoxy. Hybrid composites have mechanical properties higher than the mono-reinforced composites, consequently indicating the capability of hybridization, where the presence of beeswax can significantly improving the elastic modulus by 67% and 101% for the 2% wollastonite loading with a 4:1 and 2:1 ratio of wax beeswax respectively. The results for composites, reinforced Hybrid filler were prepared by introducing different percentages of beeswax with epoxy composite reinforced with 2% wollastonite, showed a great enhancement in elastic recovery.

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ACKNOWLEDGEMENTS

The authors are grateful to the Polymer and Petrochemical Industry, College of Material, University of Babylon for support and infrastructures provided to carry out this research.

REFERENCES

1. Alok, S., Singh, S., Kumar, A. (2013). Study of Mechanical Properties and Absorption Behaviour of Coconut Shell Powder-Epoxy Composites. *International Journal of Materials Science and Applications*, 2, 157-161.
2. Chiang, C.-L., & Hsu S.-W. (2010). Novel epoxy/expandable graphite halogen-free flame retardant composites—Preparation, characterization, and properties. *J. Polym. Res.*, 17, 315–323.
3. Davoodi, M. M., Sapuan, S. M., Ahmad, D., Ali, A., Khalina, A., Jonoobi, M. (2010). Mechanical properties of hybrid kenaf/glass reinforced epoxy composite for passenger car bumper beam. *Mater. Des.*, 31, 4927–4932.
4. Gururaja, M.N., Hari Rao, A.N. (2012). A review on recent applications and future prospectus of hybrid composites. *Int. J. Soft Comput. Eng.*, 1, 352–355.

5. Joshi, H., & Purnima, J. (2010). Development of glass fiber, wollastonite reinforced polypropylene hybrid composite : Mechanical properties and morphology. *Mater. Sci. Eng.* 527, 1946–1951.
6. katz, H.S., & Milewski, J.V. (1987). *Hand book of fillers for plastics*, Van nostrand, Reinhold, NY.
7. Lawn, B. R., & Howes, V. R. (1981). Elastic recovery at hardness indentations. *J. Mater. Sci.*, 16, 2745–2752.
8. Lorenzo, V., Perena, J. M., Fatou, J. G. (1988). Delayed elastic recovery of hardness indentations in polyethylene. *J. Mater. Sci.*, 23, 3168–3172.
9. Panzera, T.H., Sabariz, A.L.R., Stecker, K., Borges, P.H.R., Vasconcelos, D.C.L., Wasconcelos, W.L. (2010). Mechanical properties of composite materials based on Portland cement and epoxy resin. *Ceramica*, 56, 77-82.
10. Rostamiyan, Y., Mashhadzadeh, A.H., SalmanKhani, A. (2014). Optimization of mechanical properties of epoxy-based hybrid nanocomposite: Effect of using nano silica and high-impact polystyrene by mixture design approach. *Mater. Des.*, 56, 1068–1077.
11. Thakur, V. K., Thakur, M. K., (2017). *Hybrid Polymer Composite Materials*. Copyright © Elsevier Ltd.
12. VaradaRajulu, A., BabuRao, G., Lakshminarayana, R. (2001). Miscibility of polycarbonate/epoxy resin in dichloromethane by viscosity, ultrasonic and refractive index methods. *Journal of Polymer Materials*, 23, 234-240.
13. VaradaRajulu, A., Ganga Devi, L., BabuRao, G., (2003) Miscibility studies of epoxy/unsaturated polyester resin blend in chloroform by viscosity, ultrasonic velocity, and refractive index methods. *Journal of Applied Polymer Science*, 89, 2970–2972.
14. Wang, T., Xiong, D., Zhou, T. (2010). Preparation and wear behavior of carbon/epoxy resin composites with an interpenetrating network structure derived from natural sponge. *Carbon*, 48, 2435–2441.
15. Xia, X.N., Zeng, X.L., Liu, J., Xu, W.J. (2010). Preparation and characterization of epoxy/kaolinite nanocomposites. *J. Appl. Polym. Sci.*, 118, 2461–2466.
16. Yuan, Y. C., Yin, T., Rong, M. Z., Zhang, M. Q. (2008). Self-healing in polymers and polymer composites. Concepts, realization, and outlook : A review. *Express Polymer Letters*, 2, 238–250.
17. Hemanth, R. D., Kumar, M. S., Gopinath, A., & Natrayan, L. Evaluation Of Mechanical Properties Of E-Glass And Coconut Fiber Reinforced With Polyester And Epoxy Resin Matrices. *International Journal Of Mechanical And Production Engineering Research And Development (Ijimperd) Issn (P)*, 2249-6890.